APPENDIX C TO PART 136
INDUCTIVELY COUPLED PLASMA—ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

METHOD 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 5.1 (and tests

for their presence as described in Section 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved—Those elements which will pass through a 0.45 mm membrane filter.

3.2 Suspended—Those elements which are retained by a 0.45 mm membrane filter.

3.3 Total—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Sections 9.1 and 9.2).

3.4 Total Recoverable—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 Instrumental Detection Limit—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 Instrument Check Standard—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See Section 7.6.1)

3.8 Interference Check Sample—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See Section 7.6.2.)

3.9 Quality Control Sample—A solutin obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See Section 7.6.3)

3.10 Calibration Standards—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See Section 7.4)

3.11 Linear Dynamic Range—The concentration range over which the analytical curve remains linear.

3.12 Reagent Blank—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See Section 7.5.2)

3.13 Calibration Blank—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See Section 7.5.1)

3.14 Method of Standard Addition—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See Section 10.6.1.)

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (References 7, 8 and 9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The Interference information, which was collected at the Ames Laboratory,[1] is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5% of the original determination (or within some acceptable control limit (Reference 3) that has been established for that matrix.). If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10x the instrumental detection limit (maximum 100x) to the original determination should be recovered to within 90-110% or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

CAUTION: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See Section 5.2.3).

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma—Atomic Emission Spectrometer

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply—Welding grade or better.

6.2 Operating Conditions—Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and Standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid—Conc. (sp gr 1.06).

7.1.2 Hydrochloric acid—Conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1)—Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 L.

7.1.4 Nitric acid—Conc (sp gr 1.41).

7.1.5 Nitric acid, (1+1)—Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 L.

7.2 Deionized, Distilled Water—Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (Reference 6).

7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for one hour at 105°C unless otherwise specified.

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution—Stock, 1 mL = 100 µg Al. Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.2 Antimony solution—Stock, 1 mL = 100 µg Sb. Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 Arsenic solution—Stock, 1 mL = 100 µg As. Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.4 Barium solution—Stock, 1 mL = 100 µg Ba. Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for two hours) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1000 with mL deionized, distilled water.

7.3.5 Beryllium solution—Stock, 1 mL = 100 µg Be. Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.6 Boron solution—Stock, 1 mL = 100 µg B. Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 Cadmium solution—Stock, 1 mL = 100 µg Cd. Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.8 Calcium solution—Stock, 1 mL = 100 µg Ca. Suspend 0.2498 g $CaCO_3$ dried at 180°C for one hour before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.9 Chromium solution—Stock, 1 mL = 100 µg Cr. Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.10 Cobalt solution—Stock, 1 mL = 100 µg Co. Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.11 Copper solution—Stock, 1 mL = 100 µg Cu. Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.12 Iron solution—Stock, 1 mL = 100 µg Fe. Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.13 Lead solution—Stock, 1 mL = 100 µg Pb. Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.14 Magnesium solution—Stock, 1 mL = 100 µg Mg. Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.15 Manganese solution—Stock, 1 mL = 100 µg Mn. Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1000 mL with deionized, distilled water.

7.3.16 Molybdenum solution—Stock, 1 mL = 100 µg Mo. Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1000 mL.

7.3.17 Nickel solution—Stock, 1 mL = 100 µg Ni. Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1000 mL with deionized, distilled water.

7.3.18 Potassium solution—Stock, 1 mL = 100 µg K. Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water and dilute to 1000 mL.

7.3.19 Selenium solution—Stock, 1 mL = 100 µg Se. Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1000 mL.

7.3.20 Silica solution—Stock, 1 mL = 100 µg SiO_2. Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.21 Silver solution—Stock, 1 mL = 100 µg Ag. Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1000 mL with deionized, distilled water.

7.3.22 Sodium solution—Stock, 1 mL = 100 µg Na. Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.23 Thallium solution—Stock, 1 mL = 100 µg Tl. Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.24 Vanadium solution—Stock, 1 mL = 100 µg V. Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.25 Zinc solution—Stock, 1 mL = 100 µg Zn. Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. H_3NO and dilute to 1000 mL deionized, distilled water.

7.4 Mixed Calibration Standard Solutions—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See Section 7.4.1 through 7.4.5) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HC1 and dilute to 100 mL with deionized, distilled water. (See NOTES 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See Section 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 Mixed standard solution I—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 Mixed standard solution II—Barium, copper, iron, vanadium, and cobalt.

7.4.3 Mixed standard solution III—Molybdenum, silica, arsenic, and selenium.

7.4.4 Mixed standard solution IV—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 Mixed standard solution V—Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (Section 3.13) is used in establishing the analytical curve while the reagent blank (Section 3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See NOTE 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (Section 3.7), an interference check sample (Section 3.8) and a quality control sample (Section 3.9) are also required for the analyses.

7.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See Section 12.1.1.)

7.6.2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/L or five times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met.

7.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See Section 12.1.3.)

8. Sample Handling and Preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polyproplyene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See NOTES 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45 mm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45 mm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See NOTE 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in Section 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150 mL Griffin beaker and add 4 mL conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, and 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 minutes to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See NOTE 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See NOTE 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See NOTE 5) Add 3 mL of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gently reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 minutes to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer (See NOTE 4.). Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See NOTE 6). Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be used.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in Section 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (See NOTE 5). Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer (See NOTE 4). Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10. Procedure

10.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturers recommended procedures, using the typical mixed calibration standard solutions described in Section 7.4. Flush the system with the calibration blank (Section 7.5.1) between each standard (See NOTE 7). The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.

NOTE 7: For boron concentrations greater than 500 µg/L extended flush times of one to two minutes may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (Section 7.5.1) between each sample (See NOTE 7). Analyze the instrument check standard (Section 7.6.1) and the calibration blank (Section 7.5.1) each 10 samples.

10.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (Reference 2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration cs. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B)V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

11. Calculation

11.1 Reagent blanks (Section 7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze and appropriate instrument check standard (Section 7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within F15% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (Section 7.5.1) at a frequency of 10%. The result should be within the established control limits of two standard deviations of the meal value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (Section 7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of one and a half times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (Section 7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within F15% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

13. Precision and Accuracy

13.1 An interlaboratory study of metal analyses by this method was conducted by the Quality Assurance Branch (QAB) of the Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-CI). Synthetic concentrates containing various levels of the twenty-five elements listed in Table 4 were added to reagent water, surface water, drinking water and three effluents. These samples were digested by both the total digestion procedure (Section 9.3) and the total recoverable procedure (Section 9.4). Results for both digestions for the 25 elements in reagent water are given in Table 4; results for the other matrices can be found in Reference 10.

14. References

1. Winge, R.K., Peterson, V.J., and Fassel, V.A. "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

2. Winefordner, J.D. "Trace Analysis: Spectroscopic Methods for Elements," Chemical Analysis, Vol, 46, pp. 41-42.

3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

4. Garbarino, J.R. and Taylor, H.E. "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy 33, No. 3 (1979).

5. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

6. Annual Book of ASTM Standards, Part 31.

7. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

8. "OSHA Safety and Health Standards, General Industry," (29 CFR Part 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

9. "Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

10. Maxfield R. and Minak B. "EPA Method Study 27, Method 200.7 Trace Metals by ICP," National Technical Information Service, Order No. PB 85-248-656, November 1983.

Table 1—Recommended Wavelengths[1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated Detection Limit, µg/L[2]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7

Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	[3]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[1]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See Section 5.1.1).

[2]The estimated instrumental detection limits as shown are taken from Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines, EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[3]Highly dependent on operating conditions and plasma position.

Table 2—Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level

Analyte	Wavelength, nm	Interferent-									
		A1	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.214							0.21			1.4
Antimony	206.833	0.47		2.9		0.08				0.25	0.45
Arsenic	193.696	1.3		0.44							1.1
Barium	455.403										
Beryllium	313.042									0.04	0.05
Boron	249.773	0.04				0.32					
Cadmium	226.502					0.03			0.02		
Calcium	317.933			0.08		0.01	0.01	0.04		0.03	0.03
Chromium	267.716					0.003		0.04			0.04
Cobalt	228.616			0.03		0.005			0.03	0.15	
Copper	324.754					0.003				0.05	0.02
Iron	259.940							0.12			
Lead	220.353	0.17									
Magnesium	279.079		0.02	0.11		0.13		0.25		0.07	0.12
Manganese	257.610	0.005		0.01		0.002	0.002				
Molybdenum	202.030	0.05				0.03					
Nickel	231.604										
Selenium	196.026	0.23				0.09					
Silicon	288.158			0.07							0.01
Sodium	588.995									0.08	
Thallium	190.864	0.30									
Vanadium	292.402			0.05		0.005				0.02	
Zinc	213.856				0.14				0.29		

Table 3—Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1,000
As	10	Ca	1,000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1,000
Ca	1	Mg	1,000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

Table 4—ICP Precision and Recovery Data

Analyte	Concentration µg/L	Total Digestion (Section 9.3) µg/L	Recoverable Digestion (Section 9.4) µg/L
Aluminum	69-4792	X=0.9273(C)+3.6 S=0.0559(X)+18.6 SR=0.0507(X)+3.5	X=0.9380(C)+22.1 S=0.0873(X)+31.7 SR=0.0481(X)+18.8
Antimony	77-1406	X=0.7940(C)-17.0 S=0.1556(X)-0.6 SR=0.1081(X)+3.9	X=0.8908(C)+0.9 S=0.0982(X)+8.3 SR=0.0682(X)+2.5
Arsenic	69-1887	X=1.0437(C)-12.2 S=0.1239(X)+2.4 SR=0.0874(X)+6.4	X=1.0175(C)+3.9 S=0.1288(X)+6.1 SR=0.0643(X)+10.3
Barium	9-377	X=0.7683(C)+0.47 S=0.1819(X)+2.78 SR=0.1285(X)+2.55	X=0.8380(C)+1.68 S=0.2540(X)+0.30 SR=0.0826(X)+3.54
Beryllium	3-1906	X=0.9629(C)+0.05 S=0.0136(X)+0.95 SR=0.0203(X)-0.07	X=1.0177(C)-0.55 S=0.0359(X)+0.90 SR=0.0445(X)-0.10
Boron	19-5189	X=0.8807(C)+9.0 S=0.1150(X)+14.1 SR=0.0742(X)+23.2	X=0.9676(C)+18.7 S=0.1320(X)+16.0 SR=0.0743(X)+21.1
Cadmium	9-1943	X=0.9874(C)-0.18 S=0.557(X)+2.02 SR=0.0300(X)+0.94	X=1.0137(C)-0.65 S=0.0585(X)+1.15 SR=0.332(X)+0.90
Calcium	17-47170	X=0.9182(C)-2.6 S=0.1228(X)+10.1 SR=0.0189(X)+3.7	X=0.9658(C)+0.8 S=0.0917(X)+6.9 SR=0.0327(X)+10.1
Chromium	13-1406	X=0.9544(C)+3.1 S=0.0499(X)+4.4 SR=0.0009(X)+7.9	X=1.0049(C)-1.2 S=0.0698(X)+2.8 SR=0.0571(X)+1.0
Cobalt	17-2340	X=0.9209(C)-4.5 S=0.0436(X)+3.8 SR=0.0428(X)+0.5	X=0.9278(C)-1.5 S=0.0498(X)+2.6 SR=0.0407(X)+0.4

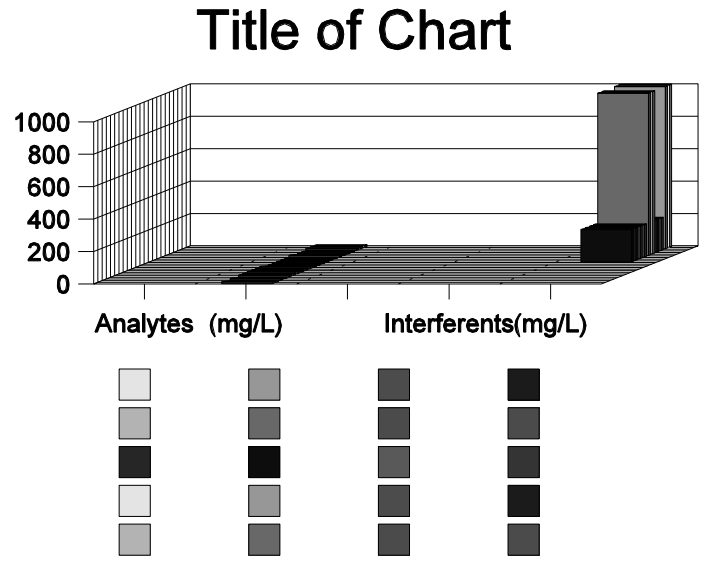

Table 4—ICP Precision and Recovery Data

Analyte	Concentration µg/L	Total Digestion (Section 9.3) µg/L	Recoverable Digestion (Section 9.4) µg/L
Copper	8-1887	X=0.9297(C)-0.30	X=0.9647(C)-3.64
		S=0.0442(X)+2.85	S=0.0497(X)+2.28
		SR=0.0128(X)+2.53	SR=0.0406(X)+0.96
Iron	13-9359	X=0.8829(C)+7.0	X=0.9830(C)+5.7
		S=0.0683(X)+11.5	S=0.1024(X)+13.0
		SR=0.0046(X)+10.0	SR=0.0790(X)+11.5
Lead	42-4717	X=0.9699(C)-2.2	X=1.0056(C)+4.1
		S=0.0558(X)+7.0	S=0.0779(X)+4.6
		SR=0.0353(X)+3.6	SR=0.0448(X)+3.5
Magnesium	34-13868	X=0.9881(C)-1.1	X=0.9879(C)+2.2
		S=0.0607(C)+11.6	S=0.0564(X)+13.2
		SR=0.0298(X)+0.6	SR=0.0268(X)+8.1
Manganese	4-1887	X=0.9417(C)+0.13	X=0.9725(C)+0.07
		S=0.0324(X)+0.88	S=0.0557(X)+0.76
		SR=0.0153(X)+0.91	SR=0.0400(X)+0.82
Molybdenum	17-1830	X=0.9682(C)+0.1	X=0.9707(C)-2.3
		S=0.0618(X)+1.6	S=0.0811(X)+3.8
		SR=0.0371(X)+2.2	SR=0.0529(X)+2.1
Nickel	17-47170	X=0.9508(C)+0.4	X=0.9869(C)+1.5
		S=0.0604(X)+4.4	S=0.0526(X)+5.5
		SR=0.0425(X)+3.6	SR=0.0393(X)+2.2
Potassium	347-14151	X=0.8669(C)-36.4	X=0.9355(C)-183.1
		S=0.0934(X)+77.8	S=0.0481(X)+177.2
		SR=0.0099(X)+144.2	SR=0.0329(X)+60.9
Selenium	69-1415	X=0.9363(C)-2.5	X=0.9737(C)-1.0
		S=0.0855(X)+17.8	S=0.1523(X)+7.8
		SR=0.0284(X)+9.3	SR=0.0443(X)+6.6
Silicon	189-9434	X=0.5742(C)-35.6	X=0.9737(C)-60.8
		S=0.4160(X)+37.8	S=0.3288(X)+46.0
		SR=0.1987(X)+8.4	SR=0.2133(X)+22.6
Silver	8-189	X=0.4466(C)+5.07	X=0.3987(C)+8.25
		S=0.5055(X)-3.05	S=0.5478(X)-3.93
		SR=0.2086(X)-1.74	SR=0.1836(X)-0.27
Sodium	35-47170	X=0.9581(C)+39.6	X=1.0526(C)+26.7
		S=0.2097(X)+33.0	S=0.1473(X)+27.4
		SR=0.0280(X)+105.8	SR=0.0884(X)+50.5
Thallium	79-1434	X=0.9020(C)-7.3	X=0.9238(C)+5.5
		S=0.1004(X)+18.3	S=0.2156(X)+5.7
		SR=0.0364(X)+11.5	SR=0.0106(X)+48.0
Vanadium	13-4698	X=0.9615(C)-2.0	X=0.9551(C)+0.4
		S=0.0618(X)+1.7	S=0.0927(X)+1.6
		SR=0.0220(X)+0.7	SR=0.0472(X)+0.5

Table 4—ICP Precision and Recovery Data

Analyte	Concentration µg/L	Total Digestion (Section 9.3) µg/L	Recoverable Digestion (Section 9.4) µg/L
Zinc	7-7076	X=0.9356(C)-0.30 S=0.0914(X)+3.75 SR=0.0130(X)+10.7	X=0.9500(C)+1.82 S=0.0597(X)+6.50 SR=0.0153(X)+7.78

AAAAX=Mean Recovery, µg/L
AAAAC=True Value for the Concentration, µg/L
AAAAS=Multi-laboratory Standard Deviation, µg/L
SR=Single-analyst Standard Deviation, µg/L

[49 FR 43431, Oct. 26, 1984; 50 FR 695, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986; 55 FR 33440, Aug. 15, 1990]